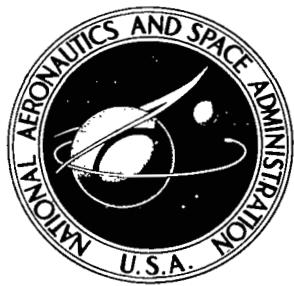


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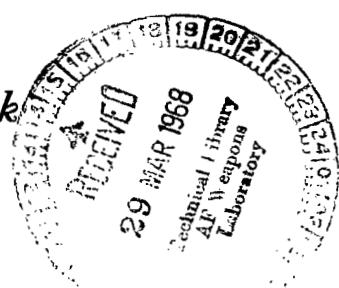
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RADIATION-INDUCED REDUCTION OF DIVALENT COPPER SALTS IN SOLUTION

by Warren H. Philipp and Stanley J. Marsik

Lewis Research Center
Cleveland, Ohio



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SUMMARY

Aqueous solutions of divalent copper salts containing soluble organic compounds were irradiated with 2-million-volt electrons. In the presence of oxidizable organic compounds (e.g., methanol, glycerine, and formaldehyde), the divalent copper ion is reduced on irradiation. From solutions of either copper(II) sulfate or copper(II) perchlorate, free copper forms, $G(\text{Cu})$ (atoms per 100 eV or 1.6×10^{-17} J) = 2.2. In solutions of copper(II) acetate and copper(II) chloride, reduction terminates with the formation of insoluble copper(I) oxide and copper(I) chloride, respectively. Irradiation of copper(II) sulfate solutions containing nonreadily oxidizable organic compounds (e.g., acetone, acetic acid, and acetonitrile) results in little or no reduction of divalent copper.

A study involving concentration parameters in the copper(II)-sulfate - methanol - water system showed that two reaction mechanisms are operative. In general, when the water is the major constituent, the initial and rate-controlling reaction is the decomposition of water by radiation to form hydrogen atoms and hydroxyl radicals. The methanol is rapidly oxidized by the hydroxyl radicals and thereby leaves an excess of reducing hydrogen radicals in the system. At high methanol concentrations, the initial process is the direct interaction of the radiation with the methanol molecules, which results in the removal of hydrogen atoms from the carbon atoms. In both mechanisms, these hydrogen atoms then reduce the divalent copper.

INTRODUCTION

The recent availability of high-energy, high-flux particle accelerators has led to extensive research in the fields of radiation damage and dosimetry. However, comparatively little work involving these particle accelerators has had preparatory chemistry for its main purpose. Henglein (refs. 1 and 2) in a recent paper describes the use of high-energy electrons for the preparation of some organic compounds in good yields. His

preparations include nitrosochloro organics, organic phosphorus dichlorides, and organic silicon trichlorides.

This report is concerned with the use of high-energy electrons for preparative chemistry, and in particular, for inorganic preparations under reducing conditions. The purpose of this investigation is to provide an understanding of the effects of some parameters involved in such preparatory radiation chemistry. Of special interest is the formation of free metals from their respective salt solutions. Although our work included the formation of free lead from aqueous lead perchlorate and free nickel from aqueous nickel sulfate buffered with sodium acetate, the scope of this report is limited to the reduction of divalent copper salts in solution. The discussions concern (1) the effect of different organic additives on the yield of copper from the irradiation of copper(II) sulfate solution; (2) the yield of copper and copper(I) compounds from salts other than copper(II) sulfate; (3) the effect of varying concentration parameters on the copper yield in the copper(II)-sulfate - methanol - water system; and (4) the mechanisms involved in these syntheses.

EXPERIMENTAL PROCEDURE

The copper salts used in this investigation were copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), copper(II) acetate ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$), copper(II) chloride (CuCl_2), copper(II) perchlorate ($\text{Cu}(\text{ClO}_4)_2$), and tetrammine copper(II) sulfate ($\text{Cu}(\text{NH}_3)_4\text{SO}_4$). In most systems studied, the solutions of copper(II) sulfate pentahydrate were used because of its solubility and the inertness of the sulfate ion toward radiation. The sulfate and the nitrate salts were commercial products. Other copper salts involved in some runs were prepared by standard techniques. Copper(II) acetate was prepared by the addition of a concentrated sodium acetate solution acidified with acetic acid to a concentrated solution of copper(II) sulfate. The insoluble copper(II) acetate was removed by filtration, and then recrystallized from dilute acetic acid. Copper(II) perchlorate and copper(II) chloride were prepared by dissolving copper(II) oxide in the stoichiometric amount of hot aqueous perchloric acid or hydrochloric acid, respectively. The tetrammine copper(II) sulfate forms when the stoichiometric quantity of ammonium hydroxide is added to a copper(II) sulfate solution.

The organic additives used were formaldehyde (CH_2O), methanol (CH_3OH), formic acid (CHOOH), acetonitrile (CH_3CN), ethanol ($\text{C}_2\text{H}_5\text{OH}$), acetic acid (CH_3COOH), trioxymethylene ($(\text{CH}_2\text{O})_3$), 2-propanol ($\text{C}_3\text{H}_7\text{OH}$), glycerine ($\text{C}_3\text{H}_5(\text{OH})_3$), acetone (CH_3COCH_3), propargyl alcohol ($\text{C}_3\text{H}_3\text{OH}$), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$), methylethyl ketone ($\text{C}_2\text{H}_5\text{COCH}_3$), mannitol ($\text{C}_6\text{H}_{12}(\text{OH})_6$), and pyrogallol ($\text{C}_6\text{H}_3(\text{OH})_3$). These additives were selected to cover the largest possible variety of functional groups and molecular structure types. Unfortunately, this choice is limited to organic compounds that are soluble in

aqueous salt solutions and at the same time do not react with the divalent copper ion without exposure to the electron beam. The organic compounds, as well as the inorganic compounds, were of high purity.

The irradiation of the solutions was done in a system (fig. 1) similar to that used by Henglein (refs. 1 and 2). The apparatus consists of a glass vessel containing the solution (about 500 ml (500 cu cm)) and of a brass ring covered by a titanium (Ti) foil (0.005 cm thick). The Ti foil serves as the inlet window for a vertical beam. This Ti window is securely cemented into the brass ring. A good seal between the brass ring and the vessel is obtained by the weight of the brass pressing an O-ring against the top edge of the vessel. Dry helium (He) passing through a glass frit of medium porosity serves to purge the system and to agitate the liquid during the irradiation. The escaping gases, leaving through the outlet tube, are passed through a bubbler and are exhausted. Cooling of the reactants is provided by immersing the vessel in a water bath. The vessel temperature is monitored throughout the irradiation by a thermocouple attached to the vessel at the solution level (about 2 cm below the top edge of the vessel).

The electron beam is furnished by an accelerator capable of supplying accelerating potentials between 0.3 to 3.0 million volts with a voltage stability greater than 99.9 percent. An arbitrary selection of 2-MeV electron (about 3.2×10^{-13} J/electron) for all irradiations proved to be a convenient choice for ease in using the equipment. A 2-million-volt electron will dissipate its energy within a depth of approximately 1 centimeter below the liquid surface. With a beam of about 4 centimeters in diameter at the surface, the reaction takes place in a cylindrical volume of about 12.5 cubic centimeters. The thorough agitation by the flowing helium assures eventual exposure of the bulk of the solution to the beam. The energy loss of a 2-million-volt electron due to absorption and scattering in the Ti window is approximately 1.5 percent (ref. 3) and is regarded as negligible in the calculations of the copper yield.

After the electron beam is aligned with the center of the entrance window, and prior to irradiation, the reaction vessel containing the solution is purged with helium. Because of practical considerations, such as heat generation and length of irradiation, a beam current of 10 to 15 microamperes was chosen. This current provides 20 to 30 watts of continuous beam power to the solution. The actual radiation dose accumulation is measured and monitored on a current indicator and integrator. The dose of about 10^{17} electrons gives a sufficient amount of product for convenient handling. Closed-circuit television allows a visual observation of both the electron beam on phosphor-coated Ti window (providing a close check on the beam alignment) and the bubbler (providing a check on agitation of the solution).

After irradiation is completed, the insoluble material is removed by filtration on a fritted glass filter, washed thoroughly with water, followed by a final wash with acetone, then dried at 110°C and weighed. The reaction product is identified by X-ray diffraction.

RESULTS AND DISCUSSION

In preliminary experiments, the irradiation of aqueous copper(II) sulfate with 2-million-volt electrons produces no apparent reaction, even when hydrogen is continuously dispersed throughout the solution. On the other hand, irradiation of copper(II) sulfate solutions containing certain organic compounds, such as methanol or ethanol, produces a significant amount of free copper.

Additional experiments, with the use of 2-million-volt electrons and methanol as the organic additive, showed that within the experimental limits (total dose of 0.030 to 0.135 C and electron current of 10 to 20 μ A), the quantity of copper produced is directly proportional to the total dose, regardless of the dose rate (electron current). Therefore, the energy yield of copper G(Cu), which is the number of copper atoms produced per 100 electron volts (1.6×10^{-17} J) of energy absorbed in the system, is independent of the total dose and electron current. For a given electron current, G(Cu) represents the rate of copper formation with respect to time; thus, G(Cu) is a convenient term to represent the relative reaction rates.

Effect of Organic Additives

Values of G(Cu) resulting from the irradiation of aqueous copper(II) sulfate solutions containing a variety of organic additives are given in table I. In general, the organic additives that give the highest G(Cu) values (1.9 to 2.4) are those that contain easily oxidizable functional groups. These compounds include ethanol (primary alcohol), 2-propanol (secondary alcohol), mannitol (polyalcohol), tetrahydrofuran (cyclic ether), and formaldehyde (aldehyde). On the other hand, acetone (ketone) and acetic acid (monocarboxylic acid, with the exception of formic acid) are not readily oxidizable because there are no hydrogen atoms "on the carbon atom already partly oxidized" (ref. 4), that is, on the carbon atom comprising the functional group. The nonoxidizable organic additives result in relatively low values of G(Cu), less than 0.1. Finally, organic additives such as acetonitrile and propargyl alcohol produce no copper.

The present hypothesis, based on dosimeter chemistry studies of the iron(III)-iron(II) system (ref. 5), states that the initial reaction step is the radiation decomposition of the water molecules into reducing hydrogen (H) atoms and into oxidizing hydroxyl (OH) radicals according to the equation



We propose that the reducing organic additives are then oxidized by OH radicals to form

stable oxidation products; thus, they are acting as OH radical scavengers. The net result is a system containing an excess of H atoms which then reduce the divalent copper. The mechanism for the oxidation of the organic reducing agent by OH radicals is probably similar to that proposed for the chemical oxidation of these organic compounds. The fact that G(Cu) is essentially the same for all these additives suggests that a reaction involving the organic additive is not the rate-controlling step in the mechanism, at least at these concentrations.

It is not surprising that nonreducing organic additives such as acetic acid and acetonitrile result in little or no copper formation. Although propargyl alcohol and pyrogallol are reported to be good reducing agents in nonradiative reactions, they are not good reducing agents for radiation chemistry in aqueous media. We attribute these nonreducing properties to the effective scavenging by these compounds of H atoms. In the case of propargyl alcohol, the H atoms are probably used up in hydrogenating the acetylenic triple bond. The fact that the presence of pyrogallol markedly inhibits the reduction of the divalent copper ion in aqueous solutions containing methanol (table I) substantiates the premise that pyrogallol does use up H atoms rather than just act as an inert species in the system.

Effect of Different Copper Salts

The results of irradiating a variety of copper salts in an aqueous solution containing methanol are given in table II. Copper(II) sulfate and copper(II) perchlorate give the same value of G(Cu). Under similar circumstances, however, copper(II) chloride is reduced to copper(I) chloride, and copper(II) acetate forms copper(I) oxide. The formation of these insoluble compounds prevents further reduction to copper; preliminary studies showed that insoluble materials do not take part in radiation reactions. The fact that these reductions stop at copper(I) indicates that the mechanism involved in the formation of copper probably goes through a univalent copper species, because in both instances the starting copper species (divalent copper ion) is the same. The value of G(Cu₂O) from aqueous copper(II) acetate is equal to the value of G(Cu) from copper(II) sulfate and copper(II) perchlorate; therefore, the overall reduction equivalent for both products is equal. These results further reveal the similarity between the two reactions. Furthermore, the free univalent copper ion is unstable with respect to the following transformation (ref. 6):



It is reasonable to assume that the deposition of copper arises from the disproportionation of the intermediate univalent copper ion.

The comparatively low value of G(Cu) obtained for the copper(II) nitrate solution is probably a result of the reduction of the nitrate anion at the expense of the divalent copper ion. With the copper(II) amine sulfate complex, no copper formed and no change was noted on irradiation. If the mechanism suggested herein is correct, obtaining free copper from this complex should not be expected; instead, the soluble copper(I) amine complex should form, which is stable to disproportionation. However, at this time no attempt was made to identify this species.

Effect of Concentration Parameters

The effect of concentration parameters on G(Cu) for the copper(II)- sulfate - methanol - water system is illustrated in figures 2 to 4. For convenience, the curves in all three figures pertain to the initial concentration. Unless specifically noted in the text, the maximum difference between the initial and final concentrations is no greater than 20 percent of the initial concentration. Of course, in the higher concentration ranges, this difference is considerably less. Thus, the general shapes of the curves as well as the numerical values are valid.

Figure 2 shows that the variation between a 0.05- and a 1.25-molar initial copper(II) sulfate concentration has only a slight effect on the value of G(Cu): thus, the reduction of the divalent copper ion to copper is not critically dependent on the divalent copper ion concentration. It should be noted that the final copper(II) sulfate concentration after the irradiation of a 0.05-molar solution was about 0.02 molar. If average concentrations instead of initial concentrations were plotted, the point at 0.05 molar would have to be placed at 0.035 molar, which would increase the concentration range over which G(Cu) does not appreciably change. Furthermore, in one experiment not shown in the figure, in which a solution containing 0.5-molar methanol and 0.025-molar initial copper(II) sulfate concentration was irradiated, the copper was almost quantitatively removed (the final divalent copper ion concentration being 0.001 M) with a G(Cu) of 1.2; this result further illustrates the relative unimportance of the divalent copper ion concentration on G(Cu). It is thereby concluded that the reaction of the divalent copper ion with the reducing species (H atoms) is not the rate-controlling step in the overall mechanism.

Figures 3 and 4 are log-log plots of G(Cu) against the concentration of methanol and water, respectively. In general, these two figures present data from the same experiments. This treatment of using two figures for the same data allows different parts of the curve to be examined in detail, which in turn facilitates the discussion of important conclusions.

Figure 3 shows that from 0.2 to 10 molar, G(Cu) is practically independent of methanol concentration; thus, over this wide concentration region, the reaction of methanol

with OH radicals is not a rate-controlling step. It appears that the initial step (reaction 1) involving the radiative decomposition of water determines the reaction rate because the variation of methanol concentration and divalent copper ion concentration has little effect on G(Cu) in this concentration region. When the methanol concentration is decreased below 0.2 molar, G(Cu) decreases at an apparently ever increasing rate. In this concentration region, it is evident that the reaction involving the scavenging of OH radicals by methanol is a rate-controlling step. Because of the continued change in the slope of the curve in the lower methanol concentration range and the lack of data pertaining to the concentration of the various species resulting from the incomplete oxidation of methanol, the order of the reaction with respect to methanol could not be determined.

The effect of water concentration on G(Cu) is best illustrated in figure 4. The value of G(Cu) increases gradually from 0.78, as the water concentration is increased to about 15 molar. From this point, G(Cu) increases more rapidly. If the decompostion of water by the interaction of the electron with the water molecules is the rate-controlling step in a certain concentration range, G(Cu) in this region would show a first-order dependence with respect to the water concentration; that is,

$$G(Cu) = KC_{H_2O}$$

and

$$\log G(Cu) = \log C_{H_2O} + \log K$$

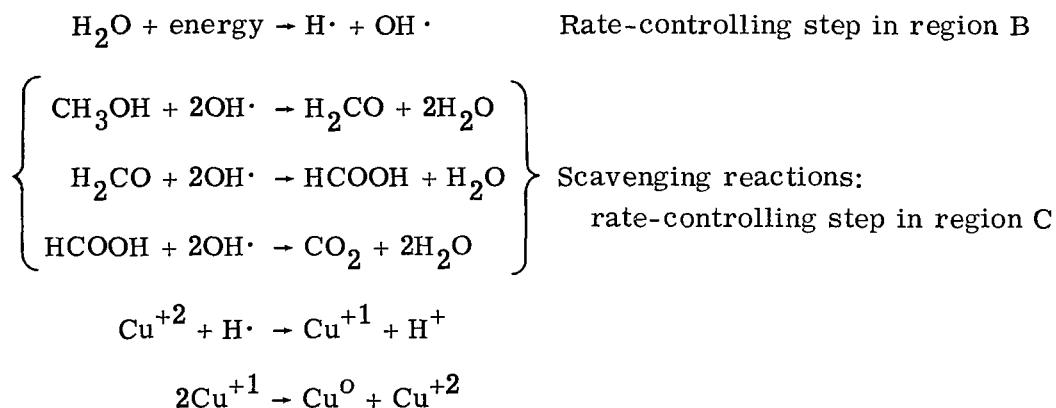
where C_{H_2O} is the water concentration and K is a rate constant. In figure 4, this first-order dependence is shown by the dashed line drawn through the portion of the experimental curve that has the expected slope very close to 1. Thus, between a 30- and 40-molar initial water concentration, the rate-controlling step is believed to be the radiative decomposition of water.

The fact that G(Cu) has a positive deviation below 30 molar requires the postulation of a second mechanism. The difference between the experimental curve and that representing the contribution of the first mechanism is shown as a dash-dot curve in figure 4. This difference curve represents a contribution from a second mechanism. For the difference curve, G(Cu) decreases with an increasing water concentration, that is, with a decreasing methanol concentration. The most likely initial reaction step for this second mechanism is the direct action of the electrons with the methanol molecules. This reaction does occur in pure methanol. The principal effect of irradiation on primary alcohols is the loss of one of the hydrogen atoms on the alpha carbon atom of the alcohol (ref. 7). Thus, it is reasonable that the divalent copper is reduced by these generated hydrogen radicals.

As the water concentration increases, so does the contribution of the OH-radical scavenger mechanism, at the expense of the mechanism involving the direct interaction of the electron with the alcohol molecules. At water concentrations above 15 molar, the importance of this scavenging mechanism increases and finally predominates at higher water concentrations. Thus, at least at relatively low concentrations of the divalent copper in solution, it is evident that the radical scavenging mechanism affords higher copper yields than does the direct interaction process. It is conceivable, however, that under certain conditions, solutions of copper compounds in organic solvents on irradiation may give higher values of G(Cu) by a direct interaction mechanism than values of G(Cu) obtained by the radical scavenging process that takes place in aqueous media. In figure 4, an extrapolation of the dashed line to pure water yields a theoretical maximum of G(Cu) = 2.7 for the ideal scavenging process.

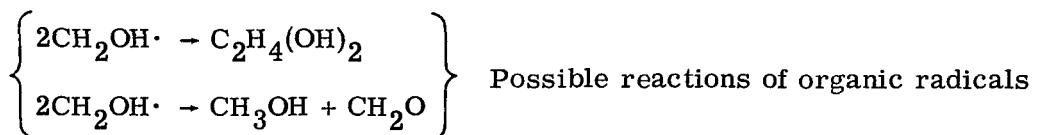
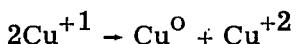
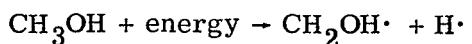
Summary of Mechanisms

The radical scavenging mechanism (the process involved when water is the major component (see regions B and C of fig. 4)) may be represented as follows, with methanol (CH_3OH) typifying the organic additive:



In an environment where a stable univalent copper species forms, the final reaction does not occur, and the end product is a univalent copper species. At a very low methanol concentration, the scavenging steps are controlling, while at somewhat higher methanol concentrations, the initial step (the decomposition of water) is rate controlling.

When the organic compound is the major component in the system (see region A of fig. 4), the initial step is believed to be the direct interaction of the radiation with the organic molecule. This direct-interaction mechanism is represented as follows with methanol typifying the organic compound:



At a water concentration of about 11 molar, the contribution from both mechanisms is equal.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 12, 1967,
129-03-15-02-22.

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TABLE I. - EFFECT OF ORGANIC ADDITIVES ON YIELD OF FREE COPPER FROM IRRADIATED
AQUEOUS COPPER(II) SULFATE SOLUTIONS

[Electron energy, 2 MeV (3.2×10^{-13} J).]

Copper sulfate concentration, moles/liter (or 10^{-3} mole/cu cm)	Additive	Additive concentration, moles/liter (or 10^{-3} mole/cu cm)	Beam current, μ A	Dose, C	Energy yield of copper, G(Cu), atoms/100 eV (or 1.6×10^{-17} J)
0.2	Formaldehyde, CH_2O	1.0	15	0.045	2.2
.5	Methanol, CH_3OH	2.0	15	.045	2.1
.1	Methanol	1.0	10	.030	2.2
.2	Methanol	.25	10	.030	2.0
.2	Formic acid, CHOOH	1.0	10	.030	1.6
.2	Acetonitrile, CH_3CN	1.0	10	.030	0.0
.5	Ethanol, $\text{C}_2\text{H}_5\text{OH}$	2.0	15	.045	2.0
.5	Acetic acid, CH_3COOH	2.0	15	.120	.022
.5	Trioxymethylene, $(\text{CH}_2\text{O})_3$ (para formaldehyde)	.67	15	.120	2.4
.2	2 Propanol, $\text{C}_3\text{H}_7\text{OH}$	1.0	10	.030	1.9
.5	Glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$	2.0	15	.090	2.3
.2	Glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$	1.0	15	.045	2.3
.5	Acetone, CH_3COCH_3	2.0	15	.090	.041
.2	Propargyl alcohol, $\text{CHC} \equiv \text{CH}_2\text{OH}$	1.0	15	.10	0.0
.2	Tetrahydrofuran, $\text{C}_4\text{H}_8\text{O}$	1.0	10	.030	2.0
.2	Methylethyl ketone, $\text{C}_2\text{H}_5\text{COCH}_3$	1.0	10	.030	.27
.5	Mannitol, $\text{C}_6\text{H}_{12}(\text{OH})_6$.5	15	.090	2.2
.5	Pyrogallol, $\text{C}_6\text{H}_3(\text{OH})_3$	1.0	15	.10	.060
.2	{Mixture of pyrogallol, $\text{C}_6\text{H}_3(\text{OH})_3$ and methanol, CH_3OH }	.5 .25	10	.030	.35

| || | |

TABLE II. - IRRADIATION OF VARIOUS COPPER(II) SALT SOLUTIONS
CONTAINING METHANOL

[Electron energy, 2 MeV (3.2×10^{-13} J); beam current, 10 μ A; dose, 0.030 C; methanol concentration, 1.0 M.]

Copper salt	Solution con- centration, moles/liter (or 10^{-3} mole/cu cm)	Product formed	Energy yield, G, molecules/100 eV (or 1.6×10^{-17} J)
Copper(II) sulfate	0.1	Copper	2.2
Copper(II) acetate	.1	Copper(I) oxide	2.2
Copper(II) nitrate	.1	Copper	.29
Copper(II) chloride	.1	Mainly copper(I) chloride ^a	----
Copper(II) perchlorate	.1	Copper	2.2
Tetrammine copper(II) sulfate	.1	No copper formed	0

^aSome insoluble copper(II) oxychlorides.

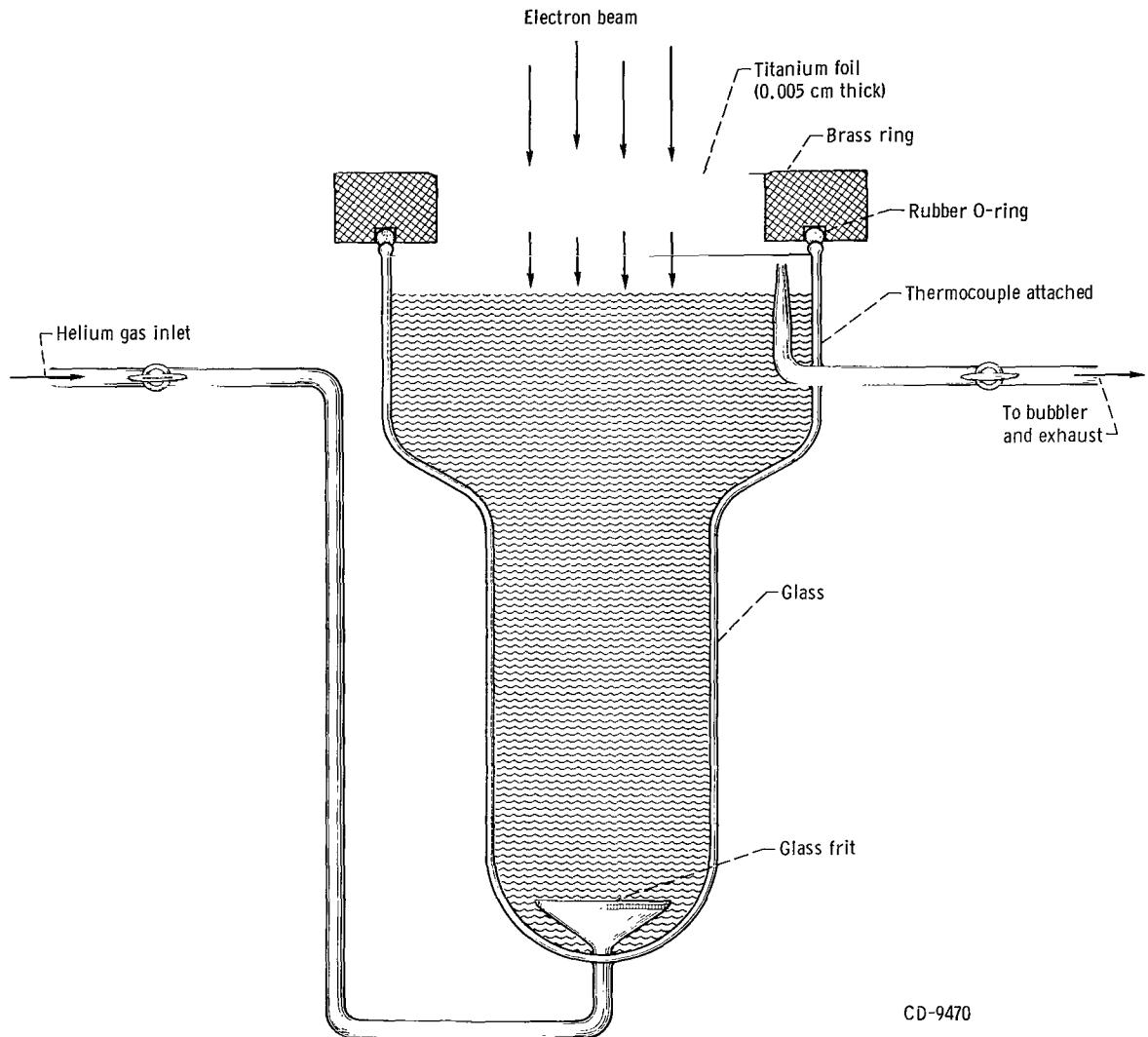


Figure 1. - Schematic drawing of irradiation vessel.

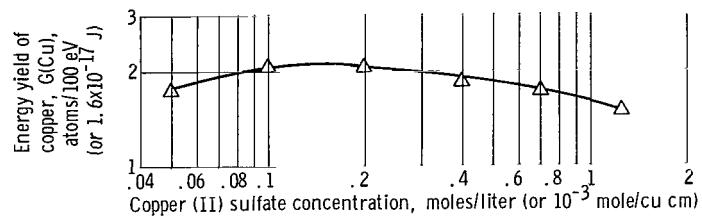


Figure 2. - Energy yield of copper as function of initial copper(II) sulfate concentration. Electron energy, 2 million electron volts (3.2×10^{-13} J); beam current, 15 microamperes; methanol concentration, 0.5 mole per liter (0.5×10^{-3} mole/cu cm).

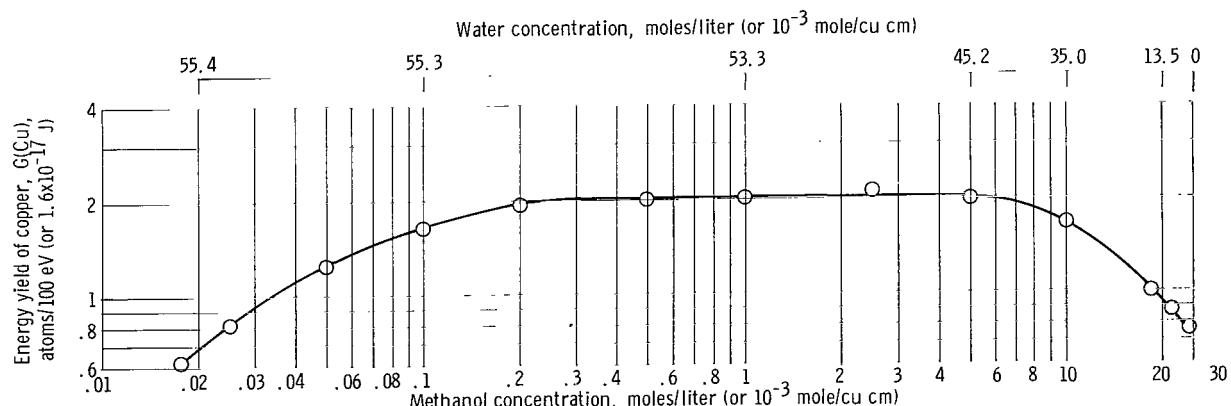


Figure 3. - Energy yield of copper as function of initial methanol concentration. Electron energy, 2 million electron volts (3.2×10^{-13} J); beam current, 15 microamperes; copper(II) sulfate concentration, 0.2 mole per liter (0.2×10^{-3} mole/cu cm).

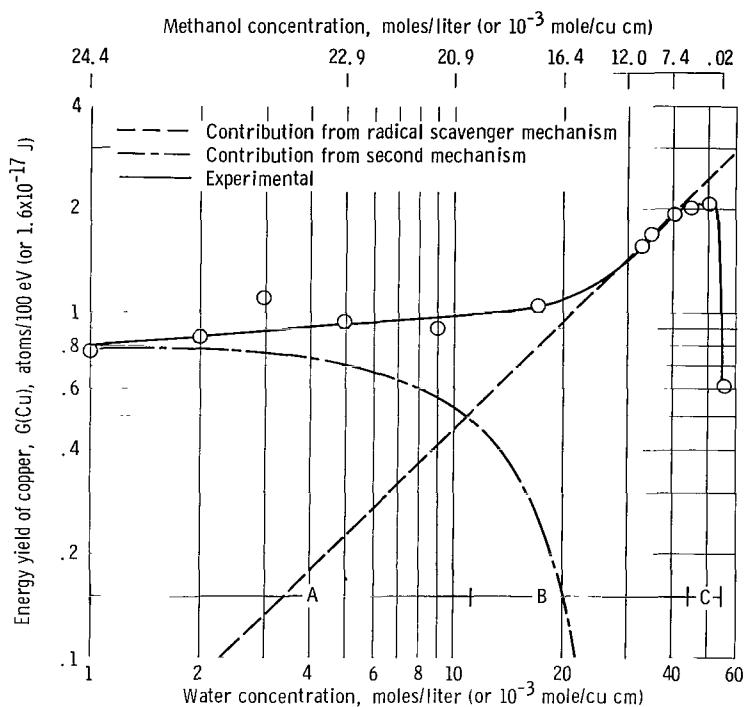


Figure 4. - Energy yield of copper as function of initial water concentration. Electron energy, 2 million electron volts (3.2×10^{-13} J); beam current, 15 microamperes; copper(II) sulfate concentration, 0.2 mole per liter (0.2×10^{-3} mole/cu cm). Region A, initial step is interaction of electron with methanol. Region B, OH radical scavenger mechanism predominates; radiative decomposition of water is the rate-controlling step. Region C, OH radical scavenger mechanism predominates; rate-controlling step is reaction of OH radicals with methanol.

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